

(12) UK Patent Application (19) GB (11) 2 134 508 A

(21) Application No **8403290** (54) **Process and composition for conditioning an aqueous system**
(22) Date of filing
24 Mar 1982
Date lodged
8 Feb 1984
(30) Priority data
(31) 8109095
(32) 24 Mar 1981
(33) United Kingdom (GB)
(43) Application published
15 Aug 1984
(51) INT CL³ **C02F 1/54**
11/14
(52) Domestic classification
C1C 210 223 230 241
253 311 320 323 324
326 331 400 40Y B
(56) Documents cited
GB A 2021551
GB 1259306
US 3953330
(58) Field of search
C1C
(60) Derived from Application
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(57) An aqueous system, for example sewage or animal farm waste, is conditioned by the addition of an alkaline earth metal hydroxide, e.g. lime; a weighting agent, e.g. calcium carbonate; and a high-molecular-weight cationic polyelectrolyte, e.g. a polyacrylamide. The hydroxide and the weighting agent are used in a weight ratio of from 9:1 to 1:9 and are preferably mixed together as an aqueous slurry before addition to the system to be conditioned.

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The date of filing shown above is that provisionally accorded to the application in accordance with the provisions of Section 15(4) of the Patents Act 1977 and is subject to ratification or amendment at a later stage of the application proceedings.

SPECIFICATION

Process and composition for conditioning an aqueous system

5 Field of the Invention

The present invention relates to a process and a composition for conditioning an aqueous system, especially a system comprising water having matter suspended therein, for example sewage.

By "conditioning" is meant bringing about a change which aids separation of water and suspended matter, as in, for example, sedimentation or filter-pressing in wastewater or sewage treatment.

Background to the Invention

Hydrated lime, hereinafter termed "lime" (calcium hydroxide) in distinction from quicklime (calcium oxide), its industrial precursor, is traditionally used in wastewater conditioning.

In industrial practice it is also known to treat aqueous particulate systems with polyelectrolytes in order to promote the flocculation of the particles. In the treatment of wastewater this enables clarification by sedimentation of the suspended matter to occur more rapidly and effectively than without the polyelectrolyte addition. In the treatment of wastewater these polyelectrolytes are often used in conjunction with a conditioning aid or destabiliser such as hydrated lime.

In wastewater treatment the use of cationic polyelectrolytes is now generally preferred, because they are directly substantive to organic suspended matter in most wastewaters: in sewage, animal farm waste, paper-making effluent and many industrial effluents, suspended matter carries a negative charge and is thus best treated by cationic polyelectrolytes which carry a positive charge.

In the treatment of potable water, lime is used as a part of a lime or lime-soda water-softening process; polyelectrolyte may be added to accelerate the sedimentation of suspended organic or inorganic matter and of the calcium carbonate particles precipitated by interaction of the lime with the hardness of the water.

30 In the above processes concerned with wastewater treatment it is advantageous to add a weighting agent which, by increasing the specific gravity of the flocculated matter, increases the rate of sedimentation and thus the rate of clarification of the liquor.

In wastewater treatment it is customary to add conditioning aids, such as lime, and polyelectrolyte separately; weighting agents where used are also separately added.

35 In the treatment of sewage and the like, various types of apparatus are used for the settling and clarifying processes. The object of these processes is to enable particles in suspension in water, that is those particles already existing in the raw water and/or those resulting from the action of a chemical reagent (added to effect, for example, coagulation, removal of iron or chemical purification), to sink to the bottom. It is possible to couple a static settling tank to a

40 flocculation unit in such processes. However, when the treatment comprises the addition of reagents, it can be an advantage to combine flocculation and clarification within a single unit, as this permits complete reaction to be obtained with the formulation of dense precipitates. Sludge-blanket clarifiers are commonly used.

In French Patent Specification 586,506 (published 25 March 1925), it is disclosed that effluent water, such as sewage, may be treated with a small quantity (generally 0.05 to 0.5%) of lime to give a flocculant precipitate that can be drained and then pressed to give a compact mass. An absorbent material, for example calcium carbonate, may be added to the lime.

Recently, P. Stead and B. Winfield, of Portsmouth Polytechnic, England, have developed a "once through" plant for the rapid sedimentation of primary sewage (i.e. sewage that has 50 passed through grit tanks) using a treatment with lime and Zetag 92 (a cationic polyacrylamide from Allied Colloids Ltd., England). The treated sewage flocculates rapidly. In a correctly designed cone-shaped treatment tank with a central downcomer, a stable sludge blanket can be formed and the effluent from the system can be maintained at a turbidity of less than 30 nephelometric units; this is accompanied by a substantial reduction in organics, phosphates and the like.

The system developed by Stead and Winfield will be of particular advantage in areas where at present virtually untreated sewage is pumped into the sea or into tidal estuaries. The plant should enable a massive reduction in pollution to be achieved at minimal cost. However, it would clearly be desirable to have available a single additive composition that could be 60 employed as a "one shot" treatment in the "once through" plant.

It is known that sewage, particularly in hard water areas, has a lime demand (or lime charge); typically, the lime demand of sewage in hard water areas is in the range of 180 to 240 ppm. Reduction in the lime charge used for treatment of the sewage gives poor results, in particular poor clarification and failure to remove organic matter. The addition of calcium carbonate, alone 65 or with a polyacrylamide, again is known to give poor results in the treatment of sewage.

- When calcium carbonate is precipitated in sewage *in situ*, using hydrated lime, either from calcium bicarbonate naturally present in the water or from calcium bicarbonate that is produced by the addition of calcium chloride or sodium bicarbonate, poor flocs and a hazy supernatant liquor are formed. The cause of this is believed to be the rapid absorption of proteins by the 5 calcium carbonate formed, this mechanism inhibiting crystal growth and floc formation. 5
- As mentioned above, it is known to use lime and Zetag 92 for the treatment of sewage. However, it would clearly be desirable to improve yet further the rate of sedimentation and the strength of the resultant floc. Any process which improves the rate of flocculation of suspended particles and increases their density and strength would be particularly applicable to processes 10 of sludge blanket clarification. 10

Summary of the invention

The present invention provides a process for conditioning an aqueous system which comprises the addition thereto of an alkaline earth metal hydroxide and a weighting agent, characterised in 15 that a high molecular weight cationic polyelectrolyte is also added to the said aqueous system and in that the weight ratio of the alkaline earth metal hydroxide to weighting agent is from 1:9 to 9:1. 15

The invention also provides a composition for use in such a process comprising an alkaline earth hydroxide and a weighting agent in a weight ratio of from 1:9 to 9:1, together with a high 20 molecular weight cationic polyelectrolyte. 20

Preferred embodiment of the invention

(I) *Applications*

The invention can be utilized to advantage in the treatment of wastewater, where it can 25 provide improved clarification, improved removal of dissolved, e.g. proteinaceous, matter, an increased sedimentation rate and increased density of the settled particulate matter. 25

The invention also permits a treatment of water, in particular potable water, in which treatment simultaneous softening (removal of calcium compounds, whether temporary or 30 permanent hardness) and flocculation of suspended impurities take place, and in which there is a more rapid sedimentation of the precipitated or flocculated matter. 30

According to another aspect there is provided a process and a material for the treatment of animal farm waste, e.g. pig farm slurry.

The invention can, furthermore, be utilized in the treatment of effluents to remove heavy 35 metals economically and effectively. The invention can also be utilized, together with the use of ferric chloride or the like, in the treatment of abattoir wastes (sewage systems). 35

However, the invention finds particular application in the treatment of sewage, whether at the primary, secondary or tertiary stages. The invention can also be used in the conditioning (including dewatering and separation) of sewage sludge.

40 As stated above, it is known that when calcium carbonate is precipitated in sewage *in situ*, there is an inhibition of crystal growth and of floc formation. However, when an insoluble carbonate is added as a weighting agent in accordance with the present invention, protein removal is still effectively maintained, but floc formation and sedimentation are improved.

45 Furthermore, it is known that a reduction in lime charge gives poor results in the treatment of sewage. However, in the practice of the present invention, it has been found that a quantity of lime can be added that is below the lime demand of the sewage whilst still obtaining excellent results. It appears that the activity of both the alkaline earth metal hydroxide and the weighting agent is enhanced when these components are added simultaneously. This enhancement of activity is especially marked when these components are mixed together, in particular as an 50 aqueous slurry, before addition to the aqueous system to be conditioned. This enhancement of activity is all the more surprising when one considers that the addition of calcium carbonate to sewage, either alone or in the presence of a polyacrylamide, is known to give very poor results. 50

(II) *Components*

The preferred compound for use as the hydroxide is hydrated lime, Ca(OH)_2 . Of course, an 55 aqueous suspension or slurry of particulate hydrated lime will generally contain some lime in solution in the interparticulate water. 55

The use of dolomitic lime (which includes magnesium compounds) or baryta (Ba(OH)_2) may be preferred on occasions.

As described in GB-A-2,095,226 (Corresponding to EP-A-0,061,354) suspensions of 60 alkaline earth metal hydroxide particles may advantageously include an anionic oligomeric polyelectrolyte as a deflocculant preferably one of high charge density, e.g. a polyacid or a salt thereof. Particularly useful as deflocculants are alkali metal salts of simple or complex oligomers of acrylic or methacrylic acid, such as Dispex N40 (Allied Colloids Ltd., U.K.) or Orotan 850 (Rohm and Haas (U.K.) Limited). These are supplied as pourable solutions of 40% and 30% 65 solids content respectively, this showing their oligomeric character. Low viscosity sodium 65

carboxymethyl cellulose such as Courlose F20 G (British Celanese Limited, U.K.), a solid product, and oligomeric sulphonates are also useful. Examples of such sulphonates are the naphthalene sulphonate/formaldehyde condensates (e.g. Dispersol T) and sulphonated melamine/formaldehyde resins (e.g. Melment); these may be used with nonionic surfactants (preferably with an HLB of 10-15), if appropriate.

The preferred weighting agents are the substantially water-insoluble carbonates. Calcium carbonate is especially preferred; this can be from a naturally occurring source, ground as appropriate, such as calcite, aragonite, limestone, coral or oyster shells, or may be from a synthetic source, for example precipitated chalk.

5 10 10 Alternatively, barium carbonate or strontium carbonate could be used. Although the present process is, in general, effective in the removal of mercaptans from an aqueous system, barium carbonate is also effective in the removal of sulphate (as is barium hydroxide). The removal of mercaptans is particularly important in the treatment of animal farm waste where the mercaptans can produce a most unpleasant odour.

15 15 15 Precipitated calcium carbonate can be prepared by the addition of calcium oxide and/or calcium hydroxide to water and treating the system with carbon dioxide. By stopping the reaction at an intermediate stage, one would obtain an aqueous slurry containing calcium hydroxide and calcium carbonate; this slurry can be used in the practice of the present invention.

20 20 20 The weight ratio of the particulate alkaline earth metal hydroxide to the weighting agent can be varied within the range from 1:9 to 9:1. However, a ratio of from 2:3 to 3:2 can give particularly good results, a ratio of 1:1 being especially preferred.

The particulate alkaline earth metal hydroxide and the weighting agent are generally added at a combined dosage rate of from 20 to 1000 ppm, preferably 20 to 300 ppm, e.g. 50 to 300 25 25 ppm. Especially in the treatment of hard-water-borne sewage, a combined dosage rate of 150 to 250 ppm, in particular 200 ppm, has been found to be very effective.

The cationic polyelectrolyte will generally have a molecular weight of at least 1×10^6 , preferably 6×10^6 and even as much as 15×10^6 . The high molecular weight is reflected in the fact that the polyelectrolyte gives appreciable viscosity in aqueous solution at a concentration of 30 only 0.1% by weight. Cationic polyacrylamides are preferred, e.g. Zetag 92 and Percol 292.

30 30 30 It is practicable to supply the lime suspensions to, for example, a sewage treatment works without a content of such a bridge-flocculating polyelectrolyte, this being added either to the lime suspension at the treatment works or separately from the lime suspension to the sewage to be conditioned, as may be found best in practice at the particular site with the particular 35 wastewater.

35 35 The cationic polyelectrolyte (which acts as a flocculant in the system to be conditioned) is generally used at a dosage rate of 0.01 ppm to 20 ppm, especially 0.05 ppm to 5 ppm.

It will be understood, of course, that the active components may each be a mixture of two or more appropriate compounds.

40 40 40 The invention is illustrated in and by the following Examples.

Example 1

Demonstration of value of lime, calcium carbonate and cationic polyelectrolyte flocculant in sewage treatment

45 45 45 A series of tests were effected in order to compare the effect on primary sewage of a treatment with hydrated lime and Zetag 92 (a cationic polyacrylamide macroelectrolyte, from Allied Colloids Limited), with a treatment employing a hydrated lime and calcium carbonate mixture and Zetag 92.

50 50 50 It is extremely difficult to use fully built slurries as a basis for laboratory jar tests since it is essential to dilute the slurries from 705 down to 1% in order accurately to dispense them into the test solutions. When active slurries are diluted flocculation will occur and thus some of the effectiveness of such a slurry is lost before it has time to react with the sewage constituents. (Here, it should be remarked that in full scale operations, the ready reactivity of the slurry is a great advantage.) To avoid problems with premature flocculation, the hydrated lime and calcium

55 55 55 carbonate were prepared as separate suspensions at a concentration of approximately 1% w/w. The required volumes of hydrated lime and calcium carbonate suspensions were pipetted into small beakers and mixed before addition to the sewage samples. After rapid mixing-in of the lime/carbonate mixture, the Zetag 92 was added with more rapid stirring for 30-60 seconds. The stirrer speed was then reduced to gentle agitation so that the floc formation could be

60 60 60 observed. After 10 minutes the stirrers were stopped and the sample was allowed to settle for 5 minutes. Turbidity and pH readings were then taken.

The following observations, *inter alia*, were made:

(ii) The mixture of hydrated lime, calcium carbonate and Zetag 92 gave excellent flocs, rapid settlement and a clear supernatant liquor. This mixture gave better results than the comparison 65 65 hydrated lime/Zetag 92 mixture, in that the resultant sludge settled more rapidly and appeared

to be stronger and more readily dewaterable than the sludge produced by the lime/Zetag 92 mixture.

(ii) The lime/carbonate/Zetag 92 mixture gave a supernatant liquor having a slightly lower pH than that produced by the comparison lime/Zetag 92 mixture.

5 (iii) The optimum weight ratio of lime to carbonate in the compositions of the present invention was about 1:1. The lime/carbonate/Zetag 92 mixture of the present invention gave good results at dosage rates ranging from 150 ppm to 250 ppm.

(iv) The presence of Dispex N40 as a deflocculant/dispersing agent in the slurries of the present invention gave no observable reduction in the effectiveness of the slurry.

10 The experimental results demonstrate that the lime/carbonate/Zetag 92 treatment, which is in accordance with the present invention, compares favourably with the treatment with lime and Zetag 92 alone. Furthermore, the mixture according to the present invention permits a considerable variation in dosage level to be tolerated with marked deterioration in the efficiency. The compositions of the present invention clearly offer increased economy and allow costs of 15 storage and dispensing equipment to be considerably reduced and will, in addition, simplify the overall treatment of the system to be conditioned

The experimental data are shown in the following tables, in which:

Table 1 summarizes a comparison of the known lime/Zetag treatment with a calcium carbonate/Zetag 92 treatment and with the lime/calcium carbonate/Zetag 92 treatment of this 20 invention;

Table 2 shows the effect of varying the dose of a 50/50 mixture of lime/carbonate and a 40/60 mixture of lime/carbonate;

Table 3 shows the effect of omitting the Dispex N40 using a 50/50 mixture of lime/carbonate; and Table 4 shows the effect of using Empycryl (Albright & Wilson) as a dispersant with a 25 50/50 mixture of lime/carbonate.

30 *Table 1*

TEST NO.	HYDRATED LIME (p.p.m.)	CALCIUM CARBONATE (p.p.m.)	FLOC RATING	SUPERNATANT	LIQUOR	35
				pH	TURBIDITY	
35	1	200	NIL	6	9.35	12
	2	180	20	5	9.4	12
	3	160	40	5	9.35	13
	4	140	60	4	9.2	14
40	5	120	80	4	9.1	14
	6	100	100	6	9.0	13
	7	100	100	6	8.9	15
	8	80	120	5	8.8	15
	9	60	140	4	8.7	20
45	10	40	160	3	8.45	25
	11	20	180	2	8.2	44
	12	NIL	200	1	7.7	82

Table 2

TEST NO.	HYDRATED LIME (p.p.m.)	CALCIUM CARBONATE (p.p.m.)	FLOC RATING	SUPERNATANT pH	LIQUOR TURBIDITY	
10	13	125	125	6	9.05	12
	14	100	100	6	8.95	16
	15	75	75	5	8.8	19
	16	100	150	6	8.9	14
	17	80	120	6	8.8	15
	18	60	90	4	8.65	19
15	<i>Table 3</i>					
	19	125	125	6	9.0	14
	20	100	100	5	8.9	14
	21	75	75	5	8.75	15
20	<i>Table 4</i>					
	22	125	125	1		80 +
	23	100	100	1		80 +
	24	75	75	1		80 +

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Notes:

1. In all tests the lime/calcium carbonate suspensions were mixed together before application. The Zetag 92 was applied last after the lime or lime/carbonate had been mixed with the sewage sample.
2. The calcium carbonate suspension in Tests 1–18 contained 0.2% Dispex N40 w/w in the weight of calcium carbonate. The calcium carbonate employed was Snowcal 6ML.
3. In all tests the charge of Zetag 92 was 0.4 ppm.
4. The "Floc Rating" was on a scale from 1 (poor) to 6 (good). A rating of 2 was considered "poor" whereas a rating of 3–5 was considered "fair".
5. The turbidity of the supernatant liquor is given in nephelometric units and was measured, as was the pH, 5 minutes after the treatment.

*Example 2**Use of lime suspensions for sewage treatment*

40 40 A series of laboratory jar flocculation tests was carried out in order to compare the effects on a primary sewage of suspensions according to the invention and of the components added as suspensions prepared directly from the dry powders. Fresh raw comminuted sewage was obtained from the Water Research Association Stevenage, U.K., and tests were carried out using a 6-jar standard laboratory flocculator with stirrers operating at the same speed in each jar

45 45 containing 500 ml of sewage. The tests were carried out by adding the conditioners or flocculants to different jars, running the stirrers at high speed for one minute and then at slow speed for ten minutes. After stopping, the formation of flocs, the rate of sedimentation and the clarity of the supernatant liquid were observed.

50 50 The dose of hydrated lime (Hydralime from Blue Circle Industries) and of polyelectrolyte (Zetag 92) to give the best clarification of the sewage was first determined in order to provide a standard. This was determined as 200 mg/l of lime or 125 mg/l of lime, and 125 mg/l of calcium carbonate (Snowcal 3ML, from Blue Circle Industries) and 0.4 mg/l of Zetag 92. The equivalent proportions of lime and Snowcal were then added as a 62% suspension (prepared by mixing 125 g of deionised water, 100 g of Snowcal 3ML whiting and 75 g of ground quicklime

55 55 A. (Stavely Lime Products Limited), stirring the mixture for 2 hours until it thickened to a paste and then adding in order 20 g of a 10% w/w solution of sodium hydroxide in deionised water and 3 g of Dispex N40). Floc formation, floc settlement and supernatant liquor clarity were similar to the standard in both cases.

It thus appeared that the content of Dispex N40 and of sodium hydroxide in the suspension investigated did not interfere with the clarification of the sewage so that the advantages of supply of lime as suspensions of increased solids content could be gained without disadvantage.

CLAIMS

1. A process for conditioning an aqueous system which comprises the addition thereto of an alkaline earth metal hydroxide and a weighting agent, characterised in that a high molecular

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weight cationic polyelectrolyte is also added to the said aqueous system and in that the weight ratio of the alkaline earth metal hydroxide to weighting agent is from 1:9 to 9:1.

2. A process according to claim 1, characterised in that the alkaline earth metal hydroxide is calcium hydroxide.

5 3. A process according to claim 1 or 2, characterised in that the weighting agent is a substantially water-insoluble carbonate.

4. A process according to claim 3, characterized in that the weighting agent is calcium carbonate.

5 5. A process according to any one of claims 1 to 4, characterised in that the weight ratio of the alkaline earth metal hydroxide to weighting agent is from 2:3 to 3:2.

10 6. A process according to any of claims 1 to 5, characterised in that the alkaline earth metal hydroxide and the weighting agent are added simultaneously to the said aqueous system.

7. A process according to claim 6, characterised in that the alkaline earth metal hydroxide and the weighting agent are mixed together before addition to the said aqueous system.

15 8. A process according to claim 6 or 7, characterised in that the alkaline earth metal hydroxide, weighting agent and high-molecular-weight cationic polyelectrolyte are added simultaneously to the said aqueous system.

9. A process according to claim 8, characterised in that the high-molecular-weight cationic polyelectrolyte, alkaline earth metal hydroxide and weighting agent are mixed together before 20 addition to the said aqueous system.

10. A process according to any one of claims 1 to 9, characterised in that the high-molecular-weight, cationic polyelectrolyte is a polyacrylamide.

11. A process according to any one of claims 1 to 10, characterised in that the alkaline earth metal hydroxide and weighting agent are added to the aqueous system to be conditioned 25 at a combined dosage rate of from 20 ppm to 1000 ppm.

12. A process according to any one of claims 1 to 11, characterised in that the cationic polyelectrolyte is added to the aqueous system to be treated at a dosage rate of 0.01 ppm to 20 ppm.

13. A process according to any one of claims 1 to 12, characterised in that the aqueous 30 system to be conditioned comprises sewage.

14. A composition for use in a process according to any one of claims 1 to 13, containing an alkaline earth metal hydroxide and a weighting agent, characterised in that it also contains a high molecular weight, cationic polyelectrolyte and in that the weight ratio of the alkaline earth metal hydroxide to weighting agent is from 1:9 to 9:1.

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